Formation and Structural Transition of Molecular Self-assembly on Solid Surface Investigated by STM

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Nanoscience and nanotechnology is the creation and utilization of materials, devices, and systems through the control of matter on the nanometer-scale. Its essence is the ability to work at these levels to generate larger structures exhibiting novel physical, chemical, and biological properties and phenomena. The aim of nanoscience and nanotechnology is to learn to exploit these properties and efficiently manufacture and employ the structures. The control of matter on nanoscale has already played an important role in scientific disciplines as diverse as physics, chemistry, materials science, biology, medicine, engineering, and computer simulation.

The well-defined nanostructure can be constructed on solid surfaces or at solid/liquid interface under potential control with inorganic ions, organic molecules or other objects. The molecular orientation and structure could be controlled by applying an electrode potential in electrolyte solution. The formation process of nanostructure could be monitored by electrochemical scanning tunneling microscopy (ECSTM). The spontaneous formation of ordered self-assembled monolayers on solid supports is not only an intriguing subject for fundamental surface science study, but also closely related to many emerging technologically important applications, especially in the field of molecular electronics. With the help of STM at sub-molecular resolution, the detailed structural information within the self-assembly monolayers can be obtained, which allows us to have an insight into how the interplay between intermolecular weak interactions and the substrate-molecule interactions governs the formation of molecular self-assembly.

In this presentation, we will describe the effect of subtle difference in the molecular structures on the organization of the molecules in the self-assembly. Understanding the weak interactions controlling the organization of molecules on solid surface provides us good opportunity to fabricate the sophisticated architectures. Finally, some future directions in the field are outlined.

We employed self-assembling and electrochemical techniques to construct two-dimensional organic molecular adlayers on HOPG and various solid surfaces. The structural details of the adlayers have been investigated by using STM and IR spectroscopy. For example[1], the self-assembly of 2, 3, 6, 7, 10, 11-hexakisalkoxy-substituted triphenylenes with n-carbon side chains (n equals 10, 12, 14, 16, 18, 20) on graphite has been investigated. Submolecular features of the molecular cores and the alkyl parts are clearly visible as shown in Fig. 1.

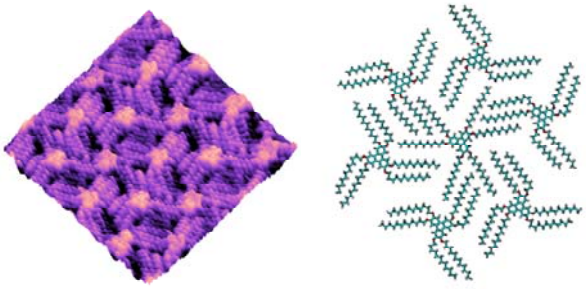

Fig. 1. High-resolution STM image of self-assembly of 2, 3, 6, 7, 10, 11-hexakisalkoxy-substituted triphenylenes with 12-carbon side chains on graphite surface. The molecule bearing a larger core tends to exhibit its three-fold symmetry in the assembling structure showing a hexagonal structure.

The results show different alkyl substitutions can lead to various packing patterns. The origin is considered in association with the interplay of molecular steric interaction and the 2D crystallization of alkyl parts. Using carboxyl functionalized porphyrin as building blocks, two-dimensional network was formed on HOPG in ambient.

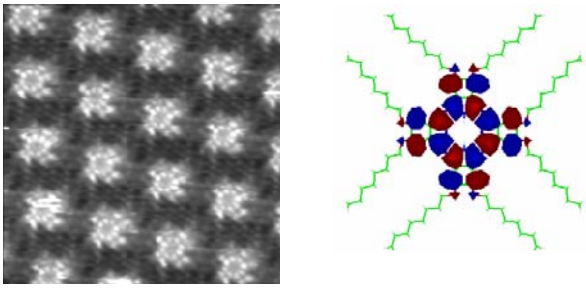

Fig. 2. High-resolution STM images of CuPcOC8 on HOPG surface. (a, left) Tunneling conditions: 909 pA, -582 mV; scan area, 12.8 nm×12.8 nm. (b,right) HOMO

Fig. 2a shows high-resolution STM images of CuPcOC8.[2] For the images at negative sample bias, the submolecular structure of individual molecules (Fig. 1a) can be clearly resolved. The inner ring of the molecule is formed by eight symmetrical bright spots, which are attributed to the conjugated phthalocyanine ring. The surrounding lobelike regions are associated with the phenyl groups of the phthalocyanine. The calculation of the electronic structure of copper phthalocyanine agrees very well with the D_{4h} symmetry of the molecular structure determined from X-ray diffraction data. Fig. 1b illustrates the charge density contours of the HOMO of the copper phthalocyanine core, calculated by ZINDO/1. A certain resemblance between the calculated

charge density distributions for the observed STM images can be observed. These calculations are helpful in analyzing the fine features and the dimensions of the observed molecules.

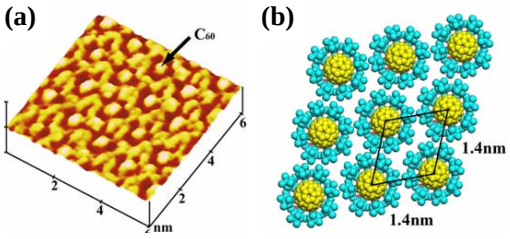

Fig. 3. (a) High-resolution STM image of calix[8]arene/C_{60} on Au(111) surface and (b) the structural model of the compound adlayer

Taking calix[8]arene/C_{60} complex as an example shown in Fig. 3, the assembly of the fullerene-based supramolecular systems was prepared. A highly ordered array of C_{60} was constructed using the calix[8]arene array as a porous template. It is demonstrated experimentally that the C_{60} is at the geometric center of the calix[8]arene for the first time. The work provides a novel method for the preparation of ordered arrays of the fullerenes. Fig.3 show the high-resolution STM image of calix[8]arene/C_{60} on Au(111) surface and the structural model of the adlayer, respectively.[3] The schematic illustration of the three adlayers are also proposed.

The results mentioned here only provide a cursory browse of some progress on constructing surface molecular nanostructures and at the same time show the possibility to detect molecular properties with atomic precision. However, it can be predicted that as the accumulation of understandings of the rules in the nanoscale, more precise control on the construction of molecular nanostructures could be expected.

ACKNOWLEDGMENT

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